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(54) LIQUID CRYSTALLINE RESIN COMPOSITION

(57)Abstract:

PURPOSE: To obtain the subject composition which is useful as an engineering plastic because of its excellent heat resistance, fluidity, mechanical properties, dimensional accuracy, particularly reduced molding flash, lowered warpage and impact resistance.

CONSTITUTION: 100 pts.wt. of a liquid-crystalline polyester and/ or liquid- crystalline polyester amide both capable of forming anisotropic melt phase are combined with 1 to 300 pts.wt. of a graphite of more than 98% fixed carbon content, 80 to 95% crystallinity and 20 to 2,000 μ m average particle size to give the objective liquid-crystalline resin composition.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the liquid crystallinity resin composition which can give the mold goods where the moldability (right mobility), dimensional stability (low camber nature, low barricade nature), and shock resistance which have the outstanding heat resistance, mechanical property, and abrasion resistance, and divided and were excellent were balanced, and which were excellent.

[0002]

[Description of the Prior Art]Although the demand to highly-efficient-izing of a plastic increases increasingly, many polymers which have various new performances are developed and the commercial scene is presented in recent years, it is observed the mobility in which the liquid crystalline polymer of the optical anisotropy characterized by the parallel arrangement of a chain was especially excellent, and in that it has mechanical properties.

[0003]The liquid crystalline polymer which carried out copolymerization of the polyethylene terephthalate, for example to para-hydroxybenzoic acid as a polymer which forms an anisotropic melt phase (JP,49-72393,A), The liquid crystalline polymer which carried out copolymerization of para-hydroxybenzoic acid and the 6-hydroxy-2-naphthoic acid (JP,54-77691,A), To para-hydroxybenzoic acid, 4,4'-dihydroxybiphenyl and terephthalic acid, The liquid crystalline polymer which carried out copolymerization of the isophthalic acid (JP,57-24407,B), The liquid crystal polyester amide generated from 6-hydroxy-2-naphthoic acid, and p-aminophenol and terephthalic acid (JP,57-172921,A), The liquid crystal polyester amide (JP,64-33123,A) etc. which were generated from para-hydroxybenzoic acid, 4,4'-dihydroxybiphenyl and terephthalic acid, p-aminobenzoic acid, and polyethylene terephthalate are indicated.

[0004]However, it is also known well that these liquid crystalline polymers have the fault that

the mechanical strength of rectangular directions and the difference of molding shrinkage are large, namely, mechanical anisotropy and size anisotropy are very large, in a flow direction and a flow direction. Since especially the liquid crystalline polymer was excellent in mobility and mechanical properties, it was mostly used as mold goods of thin meat, but anisotropy had the problem of becoming large, so that mold goods became thin meat. As a method of improving, these faults For example, 27 rubber digests, No. 8, the method of adding glass fiber to 7-14 pages (1975) at a liquid crystalline polymer, In order to improve anisotropy to a liquid crystalline polymer at JP,63-146959,A Mica, To the method and JP,64-38464,A which blend the plate object represented by talc and graphite, a mechanical strength, Although inorganic filler content copolymerized polyester and copolymerization polyester amide by which heat resistance, a moldability, dimensional stability, surface-proof wounded nature, and anisotropy were eased were indicated, in the use of precision mold goods etc., there was still a problem by generating of a camber, etc., and it was not enough.

[0005]Although molding flowability is excellent and also the molding workability also attracts attention small as compared with resin of others [generating / of the barricade at the time of shaping], complicated-shaped mold goods of a liquid crystalline polymer are [the depressor effect of a barricade] insufficient by the shape, There were problems -- sufficient dimensional accuracy is not acquired in a precision mold-goods use etc..

[0006]Therefore, this invention makes it a technical problem to obtain the liquid crystallinity resinous product group excellent in the precision molding workability which can give the mold goods where the low camber nature which solves an above-mentioned problem, has the outstanding heat resistance, mechanical property, and abrasion resistance, and divided and was excellent, and low barricade ***** shock resistance were balanced, and which were excellent.

[0007]

[Means for Solving the Problem]This invention persons reached this invention, as a result of inquiring wholeheartedly that an aforementioned problem should be solved.

[0008]Namely, this invention receives one or more sorts of liquid crystallinity resin 100 weight sections chosen from liquid crystallinity polyester and/or liquid crystallinity polyester amide which form the (A) anisotropic melt phase, (B) Fixed carbon content is in a range whose degree of crystallinity is 80 to 95% at not less than 98%, And a liquid crystallinity resin composition in which mean particle diameter blends one to black lead 300 weight section which is 2000 micrometers or less exceeding 20 micrometers, (A) The above-mentioned liquid crystallinity resin composition which is liquid crystallinity polyester in which liquid crystallinity resin consists of a structural unit of the following (I), (II), (IV) or (I), (II), (III), and (IV), [Formula 5]

[illegible]

The image displays six chemical structures representing different aromatic groups used in the synthesis of polyimides. The structures are arranged in two rows. The first row shows p-phenylene, 1,3-phenylene, and biphenylene. The second row shows naphthalene, 4,4'-oxydiphenylene, and 4,4'-thiodiphenylene. Each structure has two single bonds extending from the ring, indicating its role as a repeating unit in a polymer chain.

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And the above-mentioned liquid crystallinity resin composition which ***** and cheats out of 200 or less weight section of bulking agents further is provided to (A) liquid crystallinity resin 100 weight section.

[0009]With liquid crystallinity polyester and liquid crystallinity polyester amide which form an anisotropic melt phase in liquid crystallinity resin used by this invention. An aromatic oxycarbonyl unit, an aromatic dioxy unit, an aromatic dicarbonyl unit, It is liquid crystallinity polyester which forms an anisotropic melt phase which consists of a structural unit chosen from an ethylene dioxy unit etc., It is the liquid crystal polyester amide which forms an anisotropic melt phase which consists of a structural unit chosen from the above-mentioned structural unit, an aromatic imino carbonyl unit, an aromaticdiimino unit, an aromatic imino oxy unit, etc. Liquid crystallinity polyester etc. which form above desirable (I), (II), (IV) or (I), (II), (III), and an anisotropic melt phase that consists of a structural unit of (IV) as an example of liquid crystallinity polyester which forms an anisotropic melt phase are mentioned.

[0010]The above-mentioned structural unit (I) is a structural unit of polyester generated from para-hydroxybenzoic acid, Structural unit (II) 4,4'-dihydroxybiphenyl, 3,3' 5,5'-tetramethyl 4,4'-dihydroxybiphenyl, Hydroquinone, t-butylhydroquinone, phenylhydroquinone, 2,6-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, A structural unit generated from an aromatic dihydroxy compound chosen from 2,2-bis(4-hydroxyphenyl)propane and 4,4'-dihydroxydiphenyl ether, Structural unit (III) a structural unit generated from ethylene glycol, Structural unit (IV) Terephthalic acid, isophthalic acid, 4,4'-diphenyldicarboxylic acid, 2,6-naphthalene dicarboxylic acid, 1,2-bis(phenoxy)ethane-4,4'-dicarboxylic acid, A structural unit generated from aromatic dicarboxylic acid chosen from 1,2-bis(2-KURORU phenoxy)ethane-4,4'-dicarboxylic acid and 4, and 4' diphenyl ether dicarboxylic acid is shown respectively.

[0011]As an example of liquid crystallinity polyester amide, Liquid crystallinity polyester amide generated from 6-hydroxy-2-naphthoic acid, and p-aminophenol and terephthalic acid, Liquid crystallinity polyester amide (JP,64-33123,A) etc. which were generated from para-hydroxybenzoic acid, 4,4'-dihydroxybiphenyl and terephthalic acid, p-aminobenzoic acid, and polyethylene terephthalate are mentioned. Liquid crystallinity polyester which can be preferably used for this invention is a copolymer which consists of the above-mentioned structural unit (I), (II), (IV) or (I), (II), (III), and (IV), and the amount of copolymerization of the above-mentioned structural unit (I), (II), (III), and (IV) is arbitrary. However, from a fluid point It is preferred that it is the following amount of copolymerization.

[0012] That is, when [75 - 93 mol% of] the above-mentioned structural unit (III) is included, 60 - 95-mol% of [(I)+(II)+(III)] of a point of heat resistance, fire retardancy, and a mechanical property to the above-mentioned structural unit [(I)+(II)] is preferred, and it is more desirable. 40 - 5-mol% of [(I)+(II)+(III)] of structural unit (III) is preferred, and it is more desirable. [25 - 7-mol% of] From a point of heat-resistant and fluid balance, mole ratios of structural unit (I) / (II) are 75 / 25 - 95/5 preferably, and are 78 / 22 - 93/7 more preferably. Structural unit (IV) is equimolar as substantially as a structural unit [(II)+(III)].

[0013] On the other hand, as for a fluid point to the above-mentioned structural unit (I), when the above-mentioned structural unit (III) is not included, it is preferred that it is 40 - 90-mol% of [(I)+(II)], it is preferred that it is [60 - 88 mol] especially %, and structural unit (IV) is equimolar as substantially as structural unit (II).

[0014] In addition to an ingredient which constitutes the above-mentioned structural unit (I) - (IV) when carrying out the polycondensation of the above-mentioned liquid crystallinity polyester which can be preferably used by this invention, 3,3'-diphenyldicarboxylic acid, Aromatic dicarboxylic acid, such as 2,2'-diphenyldicarboxylic acid, adipic acid, Aliphatic dicarboxylic acid, such as azelaic acid, sebacic acid, and dodecane dione acid, Alicyclic dicarboxylic acid, such as hexahydro terephthalic acid, KURORU hydroquinone, Methylhydroquinone, 4,4'-dihydroxy diphenylsulfone, Aromatic diol, such as a 4,4'-dihydroxydiphenyl sulfide and 4,4'-dihydroxybenzophenone, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, Aliphatic series, such as 1,4-cyclohexanediol, 1, and 4-cyclohexane dimethanol, Copolymerization of aromatic hydroxycarboxylic acid, such as alicyclic diol and m-hydroxybenzoic acid, and 2,6-hydroxynaphthoic acid, and p-aminophenol, the p-aminobenzoic acid, etc. is further carried out in the range of a few rate of a grade which does not spoil the purpose of this invention.

[0015] A manufacturing method in particular of the above-mentioned liquid crystallinity resin which can be used in this invention does not have restriction, and can be manufactured according to a polycondensation method of publicly known polyester.

[0016] For example, the above -- in manufacture of liquid crystallinity polyester used preferably, when the above-mentioned structural unit (III) is not included and (1) and (2), and structural unit (III) are included, a manufacturing method of (3) is mentioned preferably.

[0017] (1) How to manufacture by a deacetylation polycondensation reaction from aromatic dicarboxylic acid, such as a diacyl ghost of aromatic dihydroxy compounds, such as p-acetoxybenzoic acid and 4,4'-diacetoxybiphenyl, 4, and 4'-diacetoxybenzene, and terephthalic acid.

[0018] (2) How to manufacture by a deacetylation polycondensation reaction after making an acetic anhydride react to aromatic dicarboxylic acid, such as aromatic dihydroxy compounds, such as para-hydroxybenzoic acid and 4,4'-dihydroxybiphenyl, and hydroquinone, and

terephthalic acid, and acylating a phenolic hydroxyl group.

[0019](3) How to manufacture by a method of (1) or (2) under existence of bis(beta-hydroxyethyl)ester of aromatic dicarboxylic acid, such as a polymer, oligomer, or bis(beta-hydroxyethyl)terephthalate of polyester, such as polyethylene terephthalate.

[0020]Although these polycondensation reactions advance also with a non-catalyst, it may be more desirable to add metallic compounds, such as the first tin of acetic acid, tetrabutyl titanate, potassium acetate and sodium acetate, antimonous oxide, and metal magnesium.

[0021]The above-mentioned liquid crystallinity resin which can be used for this invention has what has possible measuring logarithmic viscosity in pentafluoro phenol, 0.5 or more are preferred at a value measured at 60 °C with concentration of 0.1 g/dl on that occasion, and when especially the above-mentioned structural unit (III) is included, 1.0 - 3.0 dl/g is preferred, and when the above-mentioned structural unit (III) is not included, 2.0 - 10.0 dl/g is preferred.

[0022]As for melt viscosity of liquid crystallinity resin in this invention, 10-20,000 poise is preferred, and its 20-10,000 poise is especially more preferred.

[0023]This melt viscosity is melting point (T_m)+10 °C conditions, and is the value measured with a quantity-ized type flow tester under conditions of the shear rate 1,000 (1-/second).

[0024]After observation of endothermic peak temperature T_{m1} observed here when a polymer is measured on temperature-up conditions for 20 °C from a room temperature with differential calorimetric measurement with the melting point (T_m), After carrying out temperature up to T_{m1}+20 °C temperature and holding for 5 minutes at the temperature, once cooling to a room temperature on temperature fall conditions for 20 °C, endothermic peak temperature observed when it measures on temperature-up conditions for 20 °C again is pointed out.

[0025]Fixed carbon content is in a range whose degree of crystallinity is 80 to 95% at not less than 98% as black lead used for this invention, and it is important for mean particle diameter that it is 2000 micrometers or less exceeding 20 micrometers.

[0026]Not less than 98.2% and not less than 99 more% of especially fixed carbon content is desirable not less than 98%, and at less than 98%, the shock nature of resin falls and it is not desirable.

[0027]80 to 95% and 82 to 94% of a degree of crystallinity is desirable, and at less than 80%, a relaxation effect of a camber and a barricade is not revealed, and it is not desirable. If 95% is exceeded, the shock nature of resin falls and neither is preferred.

[0028]Mean particle diameter of this black lead needs to be 2000 micrometers or less exceeding 20 micrometers, its 25-1000 micrometers are preferred, and especially its 30-500 micrometers are preferred. Although friction and abrasion characteristics are excellent in mean particle diameter by 20 micrometers or less, depressor effect of size anisotropy and barricade generating at the time of shaping and a camber relaxation effect of mold goods are not enough, and preferred. If 2000 micrometers is exceeded, a fall and appearance of not only

becoming poor but a mechanical physical property become poor, and mobility at the time of shaping is not preferred.

[0029]An addition of the above-mentioned black lead is the range of five to 80 weight section especially preferably three to 100 weight section preferably one to 200 weight section to liquid crystallinity resin 100 weight section. If depressor effect of barricade generating of an addition in less than one weight section and a camber relaxation effect of mold goods are not revealed but 200 weight sections are exceeded, it is not desirable also when it is any, since formed product appearance not only being spoiled but a mechanical characteristic falls.

[0030]Although it divides roughly into black lead and there are natural graphite and an artificial graphite in it, Especially a thing for which an artificial graphite manufactured by a method of using petroleum coke or coal corks as a raw material in this invention, adding a tar pitch etc. to this, calcinating primarily at about 800 **, and heating and graphitizing at further about 2400-3000 ** is used is preferred.

[0031]Measurement of fixed carbon content of black lead takes about 10 g of graphite powder to a crucible, and is the weight (A) is weighed precisely, you make it burn in a furnace subsequently to 815 ** set up, subsequently weight (B) of after-cooling combustion remnants is weighed precisely to a room temperature, and it asks with a following formula.) of this black lead.

[0032]Fixed-carbon-content (%) = $(B)/(A) \times 100$ and a degree of crystallinity (P) of black lead are what expressed the degree of crystalline array of empirical formula following (1) of WARREN (P_1) in units of percentage, and are $d_0 = 3.354$ and $P_1 + 3.44 (1 - P_1) \dots (1)$

d_0 : Average layer-to-layer spacing of graphite crystals (angstrom)

Grating constant (C_0) = a degree of crystallinity (P) is calculated by (2) formulas as $2 \times d_0$.

[0033]Degree of crystallinity (P) = $(6.88 - C_0)/0.173$ (%)

In here, average layer-to-layer spacing (d_0) of graphite crystals is the value which was calculated by an X-ray diffraction method, specifically filled graphite powder in a sample electrode holder made from 20mmx18mmx2mm aluminum, and was measured with a reflection method by making silicon into a correlation sample by X-ray diffractometer by Rigaku Corp.

[0034]The above-mentioned black lead used for this invention can process the surface by a publicly known coupling agent (for example, the Silang system coupling agent, a titanate system coupling agent) etc., and can also be used.

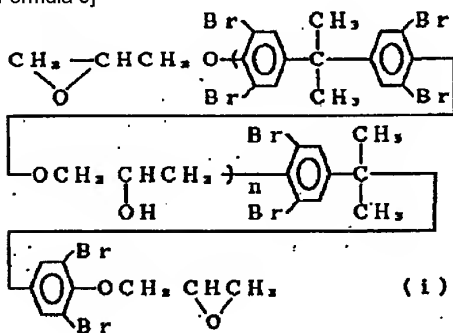
[0035]An organic bromine ghost used in this invention has especially a preferred thing of 20 % of the weight or more of bromine content including a publicly known organic bromine compound usually used as fire retardant. Specifically Hexabromobenzene, pentabromotoluene, hexabromobiphenyl, Decabromobiphenyl, a hexabromocyclodecane,

decabromodiphenyl ether, Octabromodiphenyl ether, hexabromodiphenyl ether, Bis (pentabromophenoxy)ethane, an ethylene-screw (tetrabromo phthalimide), Low-molecular-weight organic bromine compounds, such as tetrabromobisphenol A, brominated polycarbonate (for example, a polycarbonate oligomer manufactured considering bromination bisphenol A as a raw material or copolymer with the bisphenol A), A brominated epoxy compound (for example, thing epoxy compound obtained by the reaction of a diepoxy compound and bromination phenols which are manufactured by the reaction of bromination bisphenol A and epichlorohydrin, and epichlorohydrin), Poly (bromination benzyl acrylate), brominated polyphenylene ether, Polymer and oligomer which were halogenated, such as a condensate of bromination bisphenol A, cyanuric chloride, and bromination phenol, brominated polystyrene, bridge construction brominated polystyrene, and bridge construction bromination poly alpha-methylstyrene, or these mixtures are mentioned, Especially, an ethylene screw (tetrabromo phthalimide), bromination epoxy oligomer or polymer, brominated polystyrene, bridge construction brominated polystyrene, brominated polyphenylene ether, and brominated polycarbonate are preferred, and brominated polystyrene can use it most preferably.

[0036]When the above-mentioned desirable organic bromine ghost is described in more detail, what is expressed with following general formula (i) as bromination epoxy polymer is preferred.

[0037]

[Formula 9]



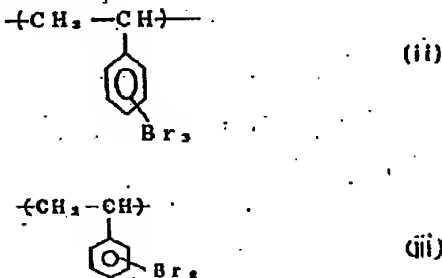
The degrees of polymerization n in the above-mentioned general formula (i) are 50-80 still more preferably 15 or more preferably.

[0038]The brominated polystyrene manufactured by brominating the polystyrene obtained by a radical polymerization or anionic polymerization as brominated polystyrene used for this invention, and bridge construction brominated polystyrene, Or although the poly bromination styrene etc. which have a bromination styrene unit expressed with a radical polymerization or

anionic polymerization, (ii) preferably manufactured by the radical polymerization, and/or a (iii) type in a bromination styrene monomer are mentioned, Poly bromination styrene of 1×10^3 - 120×10^4 has the preferred weight average molecular weight which uses as a major constituent the structural unit shown by the following (ii) and/or the (iii) type which were especially manufactured from the bromination styrene monomer.

[0039]

[Formula 10]



With the bromination styrene monomer here, that by which 2-3 bromine atoms were introduced per styrene monomer and into its aromatic ring by the substitution reaction may be preferred, and may contain 1 bromination styrene other than 2 bromination styrene and/or 3 bromination styrene, etc.

[0040]As for the above-mentioned poly bromination styrene, what contains 2 bromination styrene and/or a 3 bromination styrene unit 60% of the weight or more is preferred, and what is contained 70% of the weight or more is more preferred. It may be the poly bromination styrene which carried out copolymerization of the 1 bromination styrene 30 or less % of the weight preferably 40 or less % of the weight in addition to 2 bromination styrene and/or 3 bromination styrene. The weight average molecular weight of this poly bromination styrene has 1×10^4 - more preferred 15×10^4 . The mechanical property at the time of shaping stagnation and a solder heat resistance fall have large weight average molecular weight at less than 1×10^3 , and there is a tendency which becomes poor [the mobility of the constituent of this invention] in being larger than 120×10^4 . This weight average molecular weight is the value measured using the gel permeation chromatograph, and is a relative value of the amount standard of polystyrene molecules.

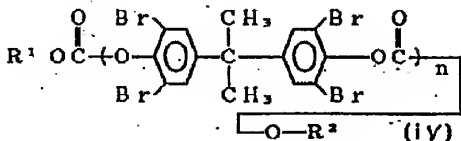
[0041]Polystyrene which brominated porosity polystyrene over which the bridge was constructed by divinylbenzene as bridge construction brominated polystyrene is preferred.

[0042]As brominated polycarbonate, what is expressed with following general formula (iv) is

preferred.

[0043]

[Formula 11]



(R1 and R2 show the aryl group which is not replaced [substitution or], and their a p-t-buthylphenyl group is the most preferred.) as the degree of polymerization n in the above-mentioned general formula (iv), four or more things are preferred -- eight or more things -- 8-25 can especially use it more preferably.

[0044]One to 30 weight section is preferred for especially the loadings of these organic bromine compounds 0.5 to 60 weight section per liquid crystallinity resin 100 weight section.

[0045]As for an organic bromine compound, in the liquid crystallinity resin composition of this invention, it is preferred to distribute with the pitch diameter of 2.5 micrometers or less in a constituent, and distributing at 2.0 micrometers or less is more preferred.

[0046]To a constituent of this invention, it is preferred to use a reinforcement and a bulking agent together, and to it as an example of a reinforcement and a bulking agent, Glass fiber, carbon fiber, aromatic polyamide textiles, a potassium titanate fiber, Gypsum fibers, brass textiles, a stainless steel fiber, steel textiles, ceramic fiber, Fibrous [such as boron whisker textiles, an asbestos fiber, mica, talc, silica, calcium carbonate, a glass bead, a glass flake, a glass micro balloon, clay, Huaras Tena lto, titanium oxide and molybdenum disulfide], powder, and a granular or tabular inorganic filler are mentioned. Even if it attaches without these bulking agents, what was processed by coupling agents, such as the Silang system and a titanate system, and other finishing agents may be used.

[0047]When adding a bulking agent, it is 200 or less weight sections to liquid crystallinity resin 100 weight section, the addition has five to 150 preferred weight section, and especially its ten to 100 weight section is preferred.

[0048]In the range which does not spoil the purpose of this invention to a liquid crystallinity resin composition of this invention. an antioxidant and a thermostabilizer (for example, hindered phenol and hydroquinone.) ultraviolet ray absorbents (for example, resorcinol.), such as phosphite and these substitution products lubricant, such as salicylate, benzotriazol, and benzophenone, and a release agent (montanic acid and its salt.) The ester, its half ester, stearyl alcohol, steer RAMIDO, polyethylene wax, etc., A usual additive agent and other thermoplastics (fluoro-resin etc.), such as colorant containing colors (for example, Nigrosine

etc.) and paints (for example, a cadmium sulfide, phthalocyanine, carbon black, etc.), a plasticizer, a fire-resistant auxiliary agent, and a spray for preventing static electricity, can be added, and the predetermined characteristic can be given.

[0049]As for a liquid crystallinity resin composition of this invention, manufacturing by melt kneading is preferred, and it can use a publicly known method for melt kneading. For example, using a Banbury mixer, a rubber roll machine, a kneader, a monopodium, or a twin screw extruder, melt kneading can be carried out at temperature of 200-400 **, and it can be considered as a constituent.

[0050]A liquid crystallinity resin composition of this invention obtained in this way Injection molding, extrusion molding, Heat resistance, a moldability, a mechanical property outstanding with the usual forming processes, such as blow molding, Three-dimensional mold goods which have surface appearance and have a mechanical property with especially small anisotropy, It is possible to process it into a sheet, a container, a pipe, etc., and For example, various gear, Various cases, a sensor, a LEP lamp, a connector, a socket, a resistor, A relay case switch, a coil bobbin, a capacitor, a variable condenser case, An optical pickup, a radiator, various tag blocks, a transformer, a plug, a printed circuit board, A tuner, a speaker, a microphone, headphone, a size motor, A magnetic head base, a power module, housing, a semiconductor, a liquid crystal, A FDD carriage, a FDD chassis, a motor brush electrode holder, An electric electronic component represented by a parabolic antenna, computer associated part, etc.; A VTR part article, A home represented by audio apparatus parts, such as television parts, an iron, a hair drier, rice cooker parts, microwave oven parts, an acoustic component, and an audio laser disc compact disk, a lighting part, refrigerator parts, air-conditioner parts, typewriter parts, word processor parts, etc., Clerical work electric product parts, an office computer associated part, a telephone associated part, A facsimile associated part, a copying machine associated part, a jig for washing, an oilless bearing, A machinery associated part represented by various bearings, such as a stern bearing and submerged bearing, a motor part article, a writer, typewriter, etc., An optical instrument, a precision instrument associated part which are represented by a microscope, binoculars, a camera, clock, etc.; An AC-dynamo terminal, An AC-dynamo connector, an I.C. regulator, a potentiometer base for light DIYA, A fuel relation, an exhaust system, and [various valves, such as an exhaust air gas valve and] suction system various pipes, An air intake nozzle snorkel, an intake manifold, a fuel pump, Engine-cooling-water joint, carburetor main body, a carburetor spacer, An exhaust gas sensor, a cooling water sensor, an oil temperature sensor, a brake pad wear sensor, A throttle position sensor, a crankshaft position sensor, An air flow meter, a brake bat wear sensor, a thermostat base for air-conditioners, a heating warm air flow control valve, a brush electrode holder for radiator motors, a water pump impeller, a turbine vein, Windshield-wiper-motor relation parts, DEYUSUTORIBYUTA, a starting switch, A starter relay, wire harness for transmission, a

window OSSHA nozzle, An air conditioning panel switch board, a coil for fuel relation electromagnetism valves, a connector for fuses, It is useful to motor vehicle associated parts, such as horn terminals, an electric equipment article electric insulating plate, a stepping motor rotor, a lamp socket, a lamp reflector, a lamp housing, a brake piston, a solenoid bobbin, an engine oil filter, and an ignition case, and other various applications.

[0051]

[Example] Hereafter, this invention is further explained in full detail according to an example.

[0052] Reference example 1 para-hydroxybenzoic-acid 994 weight section, 4,4'-dihydroxybiphenyl 126 weight section, Terephthalic acid 112 weight section and intrinsic viscosity taught polyethylene terephthalate 216 weight section of about 0.6 dl/g, and acetic anhydride 960 weight section to the reaction vessel provided with the impeller and the distillate pipe, the polycondensation was performed, the polycondensation was completed, and resin (A) was obtained. The melting point (T_m) of this resin was 314 **, and the melt viscosity in 324 ** and 1000/of shear rate second was 400 poise.

[0053] Reference example 2 para-hydroxybenzoic-acid 994 weight section, 4,4'-dihydroxybiphenyl 222 weight section, 2,6-diacetoxynaphthalene 147 weight section, acetic anhydride 1078 weight section, and terephthalic acid 299 weight section were taught to the reaction vessel provided with the impeller and the distillate pipe, the polycondensation was performed, the polycondensation was completed, and resin (B) was obtained. The melting point (T_m) of this resin was 336 **, and the melt viscosity in 346 ** and 1000/of shear rate second was 520 poise.

[0054] According to reference example 3 JP,49-72393,A, p-acetoxybenzoic acid 1296 weight and intrinsic viscosity taught polyethylene terephthalate 346 weight section of about 0.6 dl/g to the reaction vessel provided with the impeller and the distillate pipe, the polycondensation was performed, and resin (C) was obtained. The melting point (T_m) of this resin was 283 **, and the melt viscosity in 293 ** and 1000/of shear rate second was 1200 poise.

[0055] According to reference example 4 JP,54-77691,A, p-acetoxybenzoic acid 921 weight section and 6-acetoxynaphthoic acid 435 weight section were taught to the reaction vessel provided with the impeller and the distillate pipe, the polycondensation was performed, and resin (D) was obtained. The melting point (T_m) of this resin was 283 **, and was 2000 poise of melt viscosity in 293 ** and 1000/of shear rate second.

[0056] The structure of the brominated polystyrene used for reference example 5 this invention is shown in Table 1.

[0057]

[Table 1]

表 1

品 種	構 造
F R - 1	二臭素化スチレン80重量％、一臭素化スチレン15重量％、 三臭素化スチレン5重量％を含有したモノマを重合して 得たポリ臭素化スチレン（臭素含有量59％） 重量平均分子量 30×10^4
F R - 2	三臭素化スチレンモノマを重合して得たポリ臭素化スチ レン（臭素含有量68％） 重量平均分子量 30×10^4
F R - 3	ポリスチレンを臭素化して得た二臭素化ポリスチレン （臭素含有量60％） 重量平均分子量 26×10^4
F R - 4	ポリスチレンを臭素化して得た三臭素化ポリスチレン （臭素含有量68％） 重量平均分子量 25×10^4

After carrying out the dry blend of the various black lead shown in liquid crystallinity resin and Table 2 which were obtained by Examples 1-8 and the one to comparative example 9 reference examples 1-4 at a rate of Table 2, melt kneading of the cylinder temperature was carried out using the biaxial extrusion machine of 44 mmphi set as the melting point of each liquid crystallinity resin, and it was considered as the pellet.

[0058]Sumitomo nestor RUPURO mat 40 / 25 injection molding machine (made by Sumitomo Heavy Industries, Ltd.) is presented with this pellet, Shock-resistant intensity fabricated the Izod impact test specimen for cylinder temperature on with the melting point of +10 **, and a die temperature of 90 ** conditions, and Izod impact strength was measured according to ASTM D256 using these mold goods.

[0059]Cylinder temperature using a Toshiba IS55EPN injection molding machine (product made from Toshiba Machine Plastic Engineering) The melting point of +10 **, Size is 0.8-mm-thick core box mold goods [in the 8 mm/ in width / x10 mmx length 100] on condition of the injection pressure shown in the die temperature of 90 **, and Table 2, [in height] The mold goods which established a hole 450 micrometers in diameter in the pars basilaris ossis occipitalis from the gate side at 50 pieces at regular intervals were fabricated, the shaping barricade generated in the 10th hole from the gate side was observed through the profile projector, the peak of the barricade was measured like drawing 1, and the barricade was evaluated. The shaping camber generated in the flank of the mold goods was measured like drawing 2, and the camber was evaluated.

[0060]Drawing 1 shows the outline perspective view of the core box mold goods fabricated in

the example and the enlarged drawing, and the measuring point of the maximum barricade yield of a hole with a diameter of 450 micrometers of the pars basilaris ossis occipitalis. Drawing 2 shows the outline perspective view and the measuring point of a shaping camber of the core box mold goods fabricated in the example. These results were shown in Table 2.

[0061]

[Table 2]

表 2

		液晶性ポリマ		黒 鉛				耐衝撃性 Izod 衝撃強度	成形バリ		成形ソリ
		種類	配合量	固定炭素	結晶化度	粒子径	配合量		最大バリ発生量 μm		ソリ量
									射出圧力 (MPa)		mm
									49	69	
実 施 例	1	A	100	99.5	90	25	30	180	< 5	23	0.11
	2	A	100	99.5	90	75	30	173	< 5	19	0.08
	3	A	100	99.5	90	105	30	171	< 5	18	0.07
	4	A	100	99.5	90	750	30	170	< 5	15	0.07
	5	A	100	98.5	84.5	43	30	168	< 5	21	0.94
	6	B	100	99.5	90	105	30	145	7	35	0.08
	7	C	100	99.5	90	105	30	135	7	35	0.09
	8	D	100	99.5	90	105	30	115	7	35	0.09
比 較 例	1	A	100	99.5	90	7	30	182	55	105	0.30
	2	A	100	99.5	90	105	0.5	202	80	150	0.51
	3	A	100	99.5	90	105	350	21	流動性不良で成形できず		
	4	A	100	98.7	97	24	30	81	80	114	0.32
	5	A	100	98.2	75	3	30	120	70	133	0.45
	6	A	100	—	—	—	—	510	89	155	0.51
	7	B	100	—	—	—	—	450	81	157	0.52
	8	C	100	—	—	—	—	430	92	175	0.56
	9	D	100	—	—	—	—	660	81	172	0.55

注) 実施例 1～8、比較例 1～3 で使用した黒鉛は人造黒鉛、比較例 4 で使用した黒鉛は天然鱗片状黒鉛、比較例 5 で使用した黒鉛は天然土状黒鉛である。

The pellet of the constituent was manufactured like Example 3 except having blended the organic bromine compound further shown in the reference example 5 in ten to example 11 Example 3 with the rate shown in Table 3 to liquid crystallinity resin 100 weight section. They are the Sumitomo NESUTARU injection molding machine pro mats 40/25 (the Sumitomo Heavy Industries, Ltd. make is presented, and) about this pellet. The melting point of +10 ** was fabricated for the cylinder temperature, the 0.5mm(thickness) x12.7mmx127mm piece of a burning test was fabricated for the die temperature on 90 ** conditions, the vertical-type combustion test was carried out according to UL94 standard using this piece of a burning test,

and it carried out like Example 3 except having evaluated fire retardancy. These results were shown in Table 3.

[0062]

[Table 3]

表 3

		液晶性ポリマ		黒鉛			有機炭素化合物		耐衝撃性	成形バリ		機械性	成形ソリ		
		種類	配合量	固定炭素	結晶化度	粒子径	配合量	種類							
										重量部	%			μm	重量部
実施例	10	A	100	99.5	90	105	30	FR-1	3	158	< 5	17	V-0	0.08	
	11	A	100	99.5	90	105	30	FR-2	3	145	< 5	17	V-0	0.08	
	12	A	100	99.5	90	105	30	FR-3	3	110	< 5	19	V-0	0.08	
例	13	A	100	99.5	90	105	30	FR-4	3	108	< 5	19	V-0	0.09	

[0063]

[Effect of the Invention] Outstanding heat resistance, mobility to which liquid crystallinity resin

has a liquid crystallinity resin composition of this invention, Without spoiling a mechanical characteristic, since the mold goods where the low barricade nature which was excellent also in abrasion resistance, and divided and was excellent in it, low camber nature, and shock resistance were balanced and which were excellent can be given, the electrical and electric equipment and an electronic related equipment, a precision instrument related equipment, an office machine, a motor vehicle related equipment, etc. are the suitable materials for a various application.

[Translation done.]